

PATENT ABSTRACTS OF JAPAN

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(54) BIAXIALLY ORIENTED POLYESTER FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a biaxially oriented polyester film having pinhole-resistant characteristics which a biaxially oriented nylon film has and also having good moldability which a conventional biaxially oriented polyester film and the biaxially oriented nylon film have not.

SOLUTION: This biaxially oriented polyester film comprises a resin component composed of (A) 55-95 wt.% resin having 240-265°C melting point and comprising ≥ 90 wt.% polyester component composed of ethylene terephthalate and/or ethylene naphthalate and (B) 5-45 wt.% resin having 185-235°C melting point and comprising ≥ 70 wt.% polyester component, and the polyester film has properties comprising (1) ≥ 200 MPa loss modulus (E'') at a peak temperature of β disperse and (2) ≥ 140 MPa breaking strength of the film or (1') $\geq 55\%$ recovery factor of deformation of the film after 20% pulling at 0°C and (2) ≥ 140 MPa breaking strength of the film.

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CLAIMS

[Claim(s)]

[Claim 1]A biaxial orientation polyester film which resinous principles are the following (A) and (B), and is characterized by having following (1) and the characteristic of (2).

(A) The melting point. At 240-265 **, 90 % of the weight or more. Ethylene terephthalate. And/. Or the resin content 5 which 70 % of the weight or more becomes from a polyester component at 185-235 ** in 55 to 95 % of the weight of resin content (B) melting point which consists of a polyester component which comprises ethylene naphthalate - a loss modulus in peak temperature of 45-% of the weight (1) beta distribution. Breaking strength of a 200 or more MPa (2) film of (E") is 140 or more MPa. [Claim 2]A biaxial orientation polyester film which resinous principles are the following (A) and (B), and is characterized by having the following (1)' and the characteristic of (2).

(A) The melting point. At 240-265 **, 90 % of the weight or more. Ethylene terephthalate. And/. 55 to 95 % of the weight of resin content (B) melting point which consists of a polyester component which comprises ethylene naphthalate at 185-235 ** at or 0 ** of the resin content 5 which 70 % of the weight or more becomes from a polyester component - a 45-% of the weight (1)' film. Breaking strength of a not less than 55% (2) film of a modification recovery factor after 20% **** which can be set is 140 or more MPa. [Claim 3]The biaxial orientation polyester film according to claim 1 or 2 in which the melting point is characterized by 140-230 ** and a polyether unit containing denaturation polybutylene terephthalate by which copolymerization was carried out 20 to 85% of the weight one to 20% of the weight.

[Claim 4]The biaxial orientation polyester film according to claim 1 or 3, wherein an absolute value of a difference of peak temperature of beta distribution and temperature (the elevated-temperature side) of a value of a half of a loss modulus (E") in this peak temperature is not less than 30 **.

[Claim 5]The biaxial orientation polyester film according to any one of claims 1 to 4, wherein Young's modulus of a film is 2.5 - 4.0GPa.

[Claim 6]The biaxial orientation polyester film according to any one of claims 1 to 5, wherein the sum total of the degree of breaking extension of a longitudinal direction of a film and the cross direction is not less than 250%.

[Claim 7]The biaxial orientation polyester film according to any one of claims 1 to 6, wherein plane orientation coefficients of a film are 0.10-0.17.

[Claim 8]The biaxial orientation polyester film according to any one of claims 1 to 7, wherein 150 ** of a film and a heat shrinkage rate for 30 minutes are 5% or less.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]Especially this invention relates to the biaxial orientation polyester film excellent in pinhole characteristics-proof and a moldability about a biaxial orientation polyester film.

[0002]

[Description of the Prior Art]Usually, the biaxial orientation polyester film is excellent in many respects, such as the mechanical strength, thermal characteristic, and humidity characteristic, for example, is broadly used as a magnetic recording material, wrapping, etc. However, bi-oriented polyester film is inferior to a firm film, therefore pliability, and pinhole characteristics-proof, and many biaxial-stretching nylon films are used for the use than to which greater importance is attached to those characteristics.

[0003]Since a biaxial orientation polyester film was deficient in a moldability, it was rare to be used in a fabricating-operation use. Then, in order to give a moldability to a biaxial orientation polyester film, for example to JP,3-67629,A, the method of performing copolymerization in polyester is indicated.

[0004]On the other hand, there was a problem of hygroscopicity and the characteristic that a humidity expansion coefficient is large in a biaxial-stretching nylon film, and there was a problem that change of the physical properties by temporality was large, and handling was difficult. The biaxial-stretching nylon film also had the problem of being deficiently inferior to a moldability in ductility. On the other hand, both hygroscopicity and the humidity expansion coefficient of a biaxial orientation polyester film are dramatically small, and there is no problem of the humidity characteristic.

[0005]In the method of introducing a copolymerization ingredient into polyester of JP,3-67629,A, although a moldability improves, the effect of pinhole characteristics-proof like a biaxial-stretching nylon film is not given.

[0006]

[Problem(s) to be Solved by the Invention]While the purpose of this invention has pinhole characteristics-proof like a biaxial-stretching nylon film which are not in an original biaxial orientation polyester film, It is in providing the biaxial orientation polyester film which has a moldability which is not in a biaxial orientation polyester film and a biaxial-stretching nylon film.

[0007]

[Means for Solving the Problem]In order to solve an aforementioned problem, a biaxial orientation polyester film of this invention mainly has one composition of the following. Namely, a biaxial orientation

polyester film which resinous principles are the following (A) and (B), and is characterized by having following (1) and the characteristic of (2), (A) The melting point. At 240-265 **, 90 % of the weight or more. Ethylene terephthalate. And/. Or the resin content 5 which 70 % of the weight or more becomes from a polyester component at 185-235 ** in 55 to 95 % of the weight of resin content (B) melting point which consists of a polyester component which comprises ethylene naphthalate - a loss modulus in peak temperature of 45-% of the weight (1) beta distribution. (E") is (A) of the following [breaking strength / of a 200 or more MPa (2) film / resinous principle / 140 or more MPa or], and (B), and it is a biaxial orientation polyester film having the following (1)' and the characteristic of (2).

(A) The melting point. At 240-265 **, 90 % of the weight or more. Ethylene terephthalate. And/. 55 to 95 % of the weight of resin content (B) melting point which consists of a polyester component which comprises ethylene naphthalate at 185-235 ** at or 0 ** of the resin content 5 which 70 % of the weight or more becomes from a polyester component - a 45-% of the weight (1)' film. In [again] a biaxial orientation polyester film of this invention 140 or more MPa in a modification recovery factor after 20% **** which can be set, breaking strength of a not less than 55% (2) film, The melting point contains denaturation polybutylene terephthalate (the following, denaturation PBT) in which copolymerization of 140-230 ** and the polyether unit was carried out 20 to 85% of the weight one to 20% of the weight, An absolute value of a difference of peak temperature of beta distribution and temperature (elevated-temperature side) of a value of a half of a loss modulus (E") in this peak temperature is not less than 30 **, It is contained as a mode with preferred a heat shrinkage rate for that Young's modulus is 2.5 - 4.0GPa, that the sum total of the degree of breaking extension of a longitudinal direction and the cross direction is not less than 250%, that plane orientation coefficients are 0.10-0.17, 150 **, and 30 minutes being 5% or less.

[0008]

[Embodiment of the Invention]The polyester (A) and (B) which constitutes the biaxial orientation polyester film of this invention is a general term for the polymers which make main combination in a main chain an ester bond, and it can usually obtain by carrying out the polycondensation reaction of a dicarboxylic acid component and the glycol component.

[0009]As a dicarboxylic acid component used here, terephthalic acid, naphthalene dicarboxylic acid, etc. For example, isophthalic acid, diphenyldicarboxylic acid, diphenylsulfone dicarboxylic acid, Difenoxycarboxylic acid, 5-sodium sulfoisophtharate, Hydroxy acid, such as alicycle fellows dicarboxylic acid, such as aliphatic dicarboxylic acid, such as aromatic dicarboxylic acid, such as phthalic acid, oxalic acid, succinic acid, adipic acid, sebacic acid, dimer acid, maleic acid, and fumaric acid, and cyclohexylenedicarboxylic acid, and p-oxybenzoic acid, etc. can be used.

[0010]As a glycol component, everything but ethylene glycol, for example, a propanediol, Aliphatic series glycols, such as butanediol, pentanediol, hexandiol, and neopentyl glycol, Polyoxy alkylene glycol, such as aromatic glycols, such as alicycle fellows glycols, such as cyclohexane dimethanol, bisphenol A, and the bisphenol S, a diethylene glycol, a polyethylene glycol, and a polypropylene glycol, etc. can be used.

[0011]These dicarboxylic acid components and a glycol component may use two or more sorts together.

[0012]Unless the effect of this invention is checked, copolymerization of the multifunctional compounds, such as trimellitic acid, trimesic acid, and trimethylolpropane, can also be carried out, for example.

[0013]The denaturation PBT can be acquired by carrying out melt kneading of the polybutylene terephthalate and polyether which are obtained by the polycondensation reaction of the above-mentioned

statement with an extrusion machine, It can obtain by adding and carrying out the polycondensation of the polyether in the polymerization process of polybutylene terephthalate. As long as polyether here is polyoxy alkylene glycol, such as a polyethylene glycol, a polypropylene glycol, and polytetramethylene glycol, and is a range which does not spoil the effect of this invention, polyethylene terephthalate may be mixed to polyether. as for the rate to which PBT is made to carry out block copolymerization of the polyether, 20 to 85 % of the weight is preferred -- more -- desirable -- 30 to 75 % of the weight -- especially -- this -- it is 40 to 65 % of the weight preferably.

[0014]The small segment (soft segment) of a rotational hindrance is formed in a chain by carrying out block copolymerization of other polymer, especially the straight chain type polyether to polyester. The shock from the outside, the shock by bending, etc. are absorbed by the soft segment in a chain, and become the thing excellent in shock resistance and flexibility.

[0015]Polyester (A) requires that the melting point should be 240-265 **, and is 245 ** - 260 ** preferably. If heat resistance runs short at less than 240 ** and 265 ** is exceeded, since ductility falls or shock resistance falls, it is not desirable.

[0016]Polyester (B) requires that the melting point should be 185-235 **, and is 190-230 ** preferably. If heat resistance runs short, it becomes a film inferior to thermal dimensional stability in less than 185 ** and 235 ** is exceeded, since ductility falls or shock resistance falls, it is not desirable.

[0017]As for the melting point of the denaturation PBT, it is preferred that it is 140-230 **, and it is 160-190 ** especially preferably 160-210 ** more preferably. Since it is preferred to ***** denaturation PBT and to make it distribute from a point of flexibility, it is more preferred than the heat treatment temperature performed after biaxial stretching that the melting point is low temperature.

[0018]As for the polyester film of this invention, in polyester (A), polyester (B) needs to fill 5 to 45 % of the weight 55 to 95% of the weight. Polyester (A) is 65 to 85 % of the weight especially preferably 60 to 90% of the weight preferably, and polyester (B) is 15 to 35% especially preferably ten to 40% of the weight preferably. If polyester (A) exceeds less than 55 % of the weight and polyester (B) exceeds 45 % of the weight, Performances, such as mechanical strength, dimensional stability, and heat resistance, fall, and it becomes that in which the moldability which is one of the purposes of this invention is inferior, and polyester (A) exceeds 95 % of the weight, or the pinhole characteristics-proof whose polyester (B) is one of the purposes of this invention in less than 5 % of the weight are inferior.

[0019]As for the polyester film of this invention, it is preferred to contain the denaturation PBT one to 20% of the weight, and it is 5 to 15 % of the weight especially preferably three to 18% of the weight more preferably. It becomes the thing excellent in the pinhole-proof nature which is the purpose of this invention as it is this desirable range, especially flexibility, and, on the other hand, mechanical strength does not fall.

[0020]As a polymerization catalyst at the time of manufacturing the polyester used for this invention, For example, an alkali metal compound, an alkaline earth metal compound, a zinc compound, a lead compound, a manganese compound, a cobalt compound, an aluminium compound, an antimony compound, a titanium compound, etc. are mentioned, and a germanium compound, an antimony compound, and a titanium compound are used preferably. Coloration inhibitor may be used, for example, phosphorus compounds etc. can be used.

[0021]As for a polymerization catalyst and coloration inhibitor, in the arbitrary stages before completing the polymerization of polyester, adding is usually preferred. As it is indicated to the method of adding a

germanium compound granular material as it is, or JP,54-22234,B, if a germanium compound is made into an example as such a method, The method of making dissolve a germanium compound into the glycol component which is a starting material of polyester, and adding, etc. can be mentioned. As a germanium compound, for example Diacid-ized germanium, a crystal water water content germanium dioxide, Or a germaniumtetramethoxide, germaniumtetraethoxide, Germanium alkoxide compounds, such as germaniumtetrabutoxide and germanium ethylene glycoxyde, The Lynn content germanium compounds, such as germanium phenoxide compounds, such as germanium phenolate and a germanium beta-naphtho rate, germanium phosphate, and phosphorous acid germanium, acetic acid germanium, etc. can be used. Diacid-ized germanium is especially preferred. As an antimony compound, antimony oxides, such as antimonous oxide, antimony acetate, etc. can be used, for example. As a titanium compound, alkyl titanate compounds, such as tetraethyl titanate and tetrabutyl titanate, etc. are used preferably.

[0022]Further, a solid-state-polymerization reaction is carried out under decompression or an inert gas atmosphere at the temperature below the melting point, and the polyester which carries out a polycondensation reaction under an elevated temperature and decompression can decrease the content of acetaldehyde, or can be prepared in predetermined intrinsic viscosity and the amount of carboxyl end groups.

[0023]In respect of shock resistance, heat resistance, productivity, and low elution nature, 0.5 - 1 dl/g is desirable especially preferred, and the intrinsic viscosity of the polyester film of this invention is 0.55 - 0.7 dl/g.

[0024]In order to reconcile handling nature, processability, and surface Hays in the polyester film of this invention, It is preferred that the particles arbitrarily selected out of external particles, such as internal particles with a mean particle diameter of 0.01-5 micrometers, an inorganic particle, and/or organic particles, contain 0.01 to 10% of the weight, and it is preferred to contain 0.01 to 0.2% of the weight especially.

[0025]Here, as a precipitation method of internal particles, the art of a statement is mentioned, for example to JP,48-61556,A, JP,51-12860,A, JP,53-41355,A, JP,54-90397,A, etc. Concomitant use with other particles furthermore indicated to JP,55-20496,A, JP,59-204617,A, etc. can also be performed. Since it will become easy to produce defects, such as a film tear, if the particles which have the mean particle diameter over 10 micrometers are used, it is not desirable.

[0026]As said inorganic particle and/or organic particles, For example, a wet type and dry process silica, colloidal silica, aluminum silicate, The organic particles etc. which make a constituent inorganic particles, such as titanium oxide, calcium carbonate, calcium phosphate, barium sulfate, alumina, mica, kaolin, and clay, and styrene, silicone, and acrylic acid can be mentioned.

[0027]Part particles, an inorganic particle, and/or organic particles may use two or more sorts together among these. A point to the spherical particle which controls surface Hayes is preferred, and especially silica and alumina are used preferably.

[0028]In the range which does not spoil the purpose of this invention, additive agents, such as a spray for preventing static electricity, a thermostabilizer, an antioxidant, a nucleus agent, a weathering agent, an ultraviolet ray absorbent, paints, and a color, can be used for the biaxial orientation polyester film of this invention. The addition method in particular of these addition ingredients is not limited, for example, can be added in the time of solid state polymerization, or an extrusion machine etc. at the time of the melt

polymerization of polyester.

[0029]The biaxial orientation polyester film of this invention the loss modulus (E'') in the peak temperature of (1) beta distribution 200 or more MPa, It is preferably referred to as 500 or more MPa, or 300 or more MPa of modification recovery factors [400 or more MPa of] after 20% **** in (1)'0 ** are more preferably made especially into not less than 60% not less than 58% not less than 55%. It is inferior to pinhole-proof nature in the loss modulus (E'') in the peak temperature of beta distribution being less than 200 MPa, or the modification recovery factor after 20% **** at 0 ** being less than 55%.

[0030]As the technique of setting the loss modulus (E'') in the peak temperature of beta distribution to 200 or more MPa, For example, the resin (A) which consists of a polyester component by which the melting point is constituted from 240-265 **, and 90 % of the weight or more is constituted from ethylene terephthalate and/or ethylene naphthalate is blended 55 to 95% of the weight, It is effective that the melting point uses the blend polymer which blends and mixes the resin (B) in which 70 % of the weight or more consists of polyester components at 185-235 ** five to 45% of the weight. After performing biaxial stretching it not only using the above resin, but, it is preferred by giving specific energy to perform processing which improves the motility of the amorphism portion of resin. As a method of giving this energy, the additive agent which absorbs the electromagnetic waves of specified wavelengths, such as infrared rays and ultraviolet rays, can be added beforehand, and the method of irradiating with electromagnetic waves, the method of irradiating with an electron beam, the methods of heating by a specific condition, such combination, etc. can be adopted. It is effective to mix and use the resin (A) and (B) of the especially above melting points especially, and to perform heat treatment near the melting point of resin (B).

[0031]It is effective to knead an elastomer like the denaturation PBT, for example as the technique of making the modification recovery factor after 20% **** not less than 55%. It is because an elastomer is a rubber elastomer, it is what returns to the original shape when external force is removed after applying and changing external force, so the modification recovery factor after 20% **** can be enlarged if this is distributing in a film.

[0032]the absolute value of the difference of the peak temperature of beta distribution and the temperature (elevated-temperature side) of the value of the half of the loss modulus (E'') in this peak temperature is not less than 30 ** -- it is desirable and not less than 35 ** is not less than 40 ** especially preferably more preferably.

[0033]beta distribution is made into the stress relaxation by the segment in a chain, and it is thought that stress relaxation can be carried out more, so that the relaxation intensity (peak area of beta distribution) of this beta distribution is large. That is, a loss modulus (E'') becomes large what has big relaxation intensity as the broad thing of beta distribution peak, and this is considered to be greatly concerned with easing the shock from the outside, the shock by crookedness, etc.

[0034]It is preferred to perform processing which enlarges the peak area of beta distribution and an amorphism portion makes conformation change easy it not only to to make the above-mentioned resin (A) resin (B) knead in the regular range, but to take in order to get it blocked and to enlarge beta distribution intensity. For example, when manufacturing a film by the serial biaxial-stretching method extended crosswise after extending to a longitudinal direction, a longitudinal direction and the cross direction perform preheating before extension, but in order not to make conformation change of non-** control, it is preferred

to make preheat temperature higher than usual. The desirable preheat temperature of the glass transition point temperature of +25-+75 °C is [glass transition point temperature of +20-+80 °C of resin (A)] +25-+65 °C especially preferably more preferably. Preheating time is 3 to 30 seconds more preferably for 2 to 60 seconds. When preheating is extended at the temperature below this range, it will be extended in the motile low state of a chain, Therefore, if it is elongated, it becomes the structure of being hard to take conformation change, and beta distribution intensity falls and a chain is performed at the temperature beyond this range, it will be that where whose film surface the film adhered to the roll and was ruined.

[0035]An effective means also makes a crystal size small. The rate of non-¹⁰⁰ that the number of a crystal will exist mostly, that is, the way of the thing smaller than what has a large crystal size is restrained between crystals also with the same degree of crystallinity increases. Compared with a random coil-like amorphism portion, a tangle becomes empty as for this amorphism portion, it is the structure [be / nothing] which conformation change tends to take where free volume is big, therefore beta distribution intensity becomes large. By heat-treating at an elevated temperature within in 5 seconds as a method of making a crystal size small, in the case of heat treatment performed after extension, for example, although not restricted to this, . A degree of crystallinity does not have sufficient time for the crystal size of what goes up to grow, and a result and what has a small crystal size are formed. Or if optimum dose of nucleus agents are made to contain, 100-180 °C of heat treatment temperature is preferably performed in 120-160 °C and the film of the target degree of crystallinity and density is obtained, What has a small crystal size can be formed compared with the thing of the same degree of crystallinity manufactured without making a nucleus agent contain, and density, and a film with big beta distribution intensity is obtained.

[0036]The breaking strength of the biaxial orientation polyester film of this invention needs to be 140 or more MPa, and is 180 or more MPa especially preferably 160 or more MPa preferably. In less than 140 MPa, when what sharpened like the bone of a grain of rice or a fish in contents when it used, for example as wrapping is contained, a pinhole tends to be made and it is easy to produce the evil in which contents hurt or leak.

[0037]As for the Young's modulus of the biaxial orientation polyester film of this invention, it is preferred that it is 2.5 - 4.0GPa, and it is 2.9 - 3.7GPa especially preferably 2.7 to 3.8 GPa more preferably. If 4.0GPa is exceeded, it will be inferior to flexibility and a pinhole will tend to be made, and it is inferior to the flattery nature at the time of shaping, and a uniform moldability, and if it is less than 2.5 GPa, slack will tend to be possible at the time of shaping.

[0038]Next, from a point of a moldability, it is preferred that the sum total of the degree of breaking extension of the longitudinal direction of a film and the cross direction is not less than 250%, it is 280 to 700% more preferably, and the biaxial orientation polyester film of this invention is 300 to 700% especially preferably. In less than 250%, since processing suitability will fall if 700% is exceeded undesirably, since a moldability falls, it is not desirable.

[0039]moreover -- from a point of the prevention from a white blush mark at the time of shock resistance, molding workability, and bending excellent in plane orientation coefficients being 0.10-0.17, or the slack prevention at the time of elevated-temperature shaping -- desirable -- further -- desirable -- 0.10 to 0.16 -- it is 0.10-0.15 especially preferably. It is desirable for dispersion in the point which gives the flattery nature for all directions and a uniform moldability to a plane orientation coefficient to be small, It is desirable still more preferred that it is 0.02 or less, and the greatest and minimum difference of a plane orientation

coefficient at the time of measuring ten points at intervals of 3 cm about the longitudinal direction or the cross direction of a film is 0.005 or less especially preferably 0.01 or less.

[0040]Especially as a method of carrying out within the limits which described the plane orientation coefficient of the film above, although not limited, the draw magnification of the longitudinal direction of a film or the cross direction, extension temperature, a stretching speed and also heat treatment temperature, adjustment of heat treating time, etc. can attain, for example.

[0041]It is desirable still more preferred from the heat dimensional change control at the time of processing, and a point of moderate self-tension load that 150 ** and the heat shrinkage rate for 30 minutes are -1-5%, and the biaxial orientation polyester film of this invention is 0 to 4%. It is 0 to 3% especially preferably.

[0042]30 ppm or less of content [25 ppm or less of] of the acetaldehyde in [the point that the biaxial orientation polyester film of this invention makes health nature good to] a film is 20 ppm or less especially preferably still more preferably preferably. The method in particular of setting content of the acetaldehyde in a film to 30 ppm or less is not limited, For example, it can carry out by the method of carrying out solid state polymerization of the polyester at the temperature below the not less than 150 ** melting point under decompression or an inert gas atmosphere, the method of carrying out melting extrusion using a vacuum vent type extrusion machine, etc.

[0043]Although the manufacturing method of the biaxial orientation polyester film of this invention is described, it is not limited to in particular this. After drying polyester if needed, a publicly known melting extrusion machine is supplied and it extrudes from a slit shape die to a sheet shaped, and it is made to stick to a casting drum with methods, such as electrostatic impression, cooling solidification is carried out, and an unextended sheet is obtained.

[0044]This unextended sheet is extended and heat-treated [of a film / the longitudinal direction and crosswise], and the target film is obtained. What is depended on a tenter method in respect of the quality of a film is preferred, and after extending to a longitudinal direction, the simultaneous biaxial-stretching method which extends the serial biaxial-stretching method extended crosswise and a longitudinal direction, and the cross direction almost simultaneous is preferred.

[0045]As draw magnification, 1.5 to 4.0 times are preferred in each direction, and they are 1.8 to 4.0 times more preferably. The draw magnification of a longitudinal direction and the cross direction may enlarge whichever, and is good also as the same. A stretching speed has preferred 1000% 200000% part for /- and thing [a part for /]. As for extension temperature, 80-150 ** is preferred.

[0046]Although a film is heat-treated after biaxial stretching, this heat treating method in particular is not limited, but can be performed by publicly known methods, such as inside of oven, and a heated roll top. film temperature of heat treatment is [melting point-60--5 ** of resin (B)] preferred -- more -- desirable -55 --7 ** is -50--10 ** especially preferably. Heat treatment becomes what was inferior to thermal dimensional stability when melting point-less than 60 ** of resin (B) became, and at the temperature over melting point-5 ** of resin (B), property difference with the resin (A) which crystallization follows becomes large, and at the time of crookedness, stress is not applied uniformly but is inferior to pinhole characteristics-proof.

[0047]The above-mentioned heat treatment may be performed loosening a film [the / longitudinal direction and/or crosswise]. It may receive for all directions, re-extension may be performed once or more, and heat treatment may be performed after re-extension.

[0048]Although the thickness of the biaxially oriented film of this invention can be set as arbitrary thickness,

it is 10-80 micrometers that it is 3-100 micrometers desirable still more preferably, and it is 10-50 micrometers especially preferably. In less than 3 micrometers, it is inferior to mechanical strength, and when 100 micrometers is exceeded, it is inferior to flexibility.

[0049]Either a monolayer or lamination can be used for the biaxial orientation polyester film of this invention. It laminates, and when using it, polymer, such as thermoplastic polymer and thermosetting polymer, may be laminated. Especially laminated constitution is also good to laminate two-layer [which was not limited but laminated the biaxial orientation polyester film of this invention on one side], three layers laminated in the center, and two sorts or more of films, or to laminate a film to four or more layers.

[0050]The biaxial orientation polyester film of this invention can raise an adhesive property by performing surface treatments, such as corona discharge treatment, to a film. As processing strength in that case, 5 - 50 W-min/m² is preferably. It is 10 - 45 W-min/m² more preferably. Surface treatments, such as surface unevenness processing of embossing, sand mat processing, etc. or corona discharge treatment, plasma treatment, and alkali treatment, may be performed if needed.

[0051]To the biaxial orientation polyester film of this invention, an easily-adhesive processing agent, A spray for preventing static electricity, a steam and a gas barrier agent, release agents (polyvinylidene chloride etc.), Coating and printing of a binder, adhesives, fire retardant, an ultraviolet ray absorbent, a mat-ized agent, paints, a color, etc. may be performed, Vacuum deposition of metal and its compounds, such as aluminum, an aluminum oxide, oxidized silicon, and palladium, may be carried out for the purpose, such as protection from light, a steam and the gas barrier, surface conductivity, and infrared reflection, and it is not limited for the purpose and a method to these.

[0052]Although the use in particular of the biaxial orientation polyester film of this invention is not limited, it is preferably used for the object for wrapping, and fabricating operations.

[0053]Below, the measurement of each physical properties and the characteristic and the valuation method which were used for this invention are explained.

(1) The melting point (T_m), the sub endothermic peak resulting from heat treatment (T_{meta})

It measured using the differential scanning calorimeter (DSC2 by PerkinElmer, Inc.). Endothermic peak temperature accompanying crystal fusion was made into the melting point (T_m) in the process in which temperature up of 10 mg of the resin samples is carried out from 20 ** to 280 ** the speed for 10 **/under a nitrogen air current. The sub endothermic peak which originates in heat treatment in the process in which temperature up of 10 mg of the film samples is carried out from 20 ** to 280 ** the speed for 10 **/under a nitrogen air current was set to T_{meta}.

(2) Between the marked lines was taken to 10 mm in width of a modification recovery-factor film sample, and the examination length of 150 mm 100 mm, and it pulled to them 20% in 0 ** and 65%RH using the Instron type tension tester, and held to them for 30 seconds as it is, and the length between the marked lines after **** opening was measured to them, and they were asked for the modification recovery factor with the following formula.

[0054]Modification recovery factor = 1- (-100 between the after-modification marked lines) / {20} x100(3)
beta distribution peak temperature, a loss modulus (E'')

Using a dynamic viscoelasticity device ("RHEOVIBRON"DDV-II-EA made from ORIENTEC), 110 MHz of test frequencies, 16 micrometers (piece amplitude) of vibration displacement, 5 g of preliminary tension,

measurement temperature range-130 °-240 °, By heating-rate/of 2 °, it asked for the loss modulus (E'') with the sample size of 40 mm x 4 mm (longitudinal direction x cross direction), and asked for the loss modulus (E'') at the temperature of the peak resulting from beta distribution observed by 0 ° or less at this time, and peak temperature.

(4) About breaking strength breaking strength, the stress at the time of a film when measured in 25 ° and 65%RH fracturing in accordance with the method specified to JIS K 7127 using the Instron type was measured.

(5) About the elastic-modulus elastic modulus, it measured in 25 ° and 65%RH in accordance with the method specified to JIS Z 1702 using the Instron type tension tester.

(6) About ductility ductility, x(sample length of length/[which was elongated] origin) 100 when measured in 25 ° and 65%RH was made into the degree of breaking extension in accordance with the method specified to JIS K 7127 using the Instron type tension tester.

(7) Plane orientation coefficient (fn)

The refractive index (Nx, Ny, Nz) of a longitudinal direction, the cross direction, and a thickness direction was measured by having used the sodium D line as the light source using the Abbe refractometer, and it asked with the following formula.

[0055]Between the marked lines of the longitudinal direction (MD) of $fn = (Nx + Ny) / 2 - Nz$ (8) heat-shrinkage-rate film sample and the cross direction (TD) is taken to 200 mm, After having cut the film to 10-mm width, having hung the film sample in the length direction, adding 1 g of load in the length direction and heating for 30 minutes using a 190 ° hot wind, the length between the marked lines was measured and the shrinkage amount of the film was expressed in units of percentage as a rate over a full-scale method.

(9) The intrinsic viscosity film was dissolved in orthochlorophenol, and it measured in 25 °.

(10) The GERUBO tester specified to pinhole-characteristics-proof-1ASTMF-392 was used, and 500 GERUBO repetition bending tests were carried out for the film sample (280 mm x 180 mm) by 0 ° of ambient temperature. The pinhole number after an examination was measured. More than C class is success.

[0056]

A class: -- a pinhole -- 2.5 or less piece B class: -- a pinhole -- 5.5 or less piece C class: -- a pinhole -- nine or less piece D class: -- a pinhole exceeds or fractures nine pieces.

(11) It stretched so that there might be no slack by a film in a ring with pinhole-characteristics-proof-2 diameter of 40 mm, and the 60 degrees of point angle and the tip R0.5mm needle made from sapphire were used, the center of the circle was pierced the speed for 50-mm/, load in case a needle penetrates was converted into 1 mm of films, and was pierced, and it was considered as intensity. More than B class considers it as success.

[0057]

A class: -- intensity -- not less than 25kg/[mm] B class: -- intensity -- not less than 20kg/[mm] C class: -- a less than 20kg/[mm] (12) moldability tip part has hemispherical intensity (3 cm in radius). The drum section pushed into the film which slackened in the metal flask of 20 cm around, and stuck [after heating at 185 °] the metallic mold of cylindrical shape (3 cm in radius) that there is nothing, fabricated with the contraction ratio 0.8, and judged as follows. More than B class is success.

A class: It is fabricated uniformly and a Plastic solid does not have slack, either.

[0058]B class: Although there is a portion which carried out thickness deviation in part, as the whole, it is fabricated uniformly and there is also no slack after shaping.

[0059]C class: Uneven shaping is carried out clearly and that surface is accepted.

[0060]

[Example]An example explains this invention below.

(Example 1) Polyethylene terephthalate as polyester (A) 80 % of the weight, Polybutylene terephthalate was adjusted so that an alumina particle with a mean particle diameter of 0.2 micrometer might be contained for the with 18 % of the weight and a melting point of 160 ** denaturation PBT 0.05% of the weight, using 2 % of the weight as polyester (B). Having supplied the single screw extruder and carrying out electrostatic impression after the regurgitation from the usual cap, after carrying out vacuum drying of the polymer chip at 120 ** for 6 hours, cooling solidification was carried out on the mirror plane cooling drum, and the unstretched film was obtained. this unstretched film -- it extending to a longitudinal direction at the extension temperature of 88 **, extending 3.4 times crosswise at 110 ** after 3.2 time extension and within a tenter, and with a non-adhering silicone roll (hardness of 73 degrees), [rank second and] By carrying out crosswise relaxed 4%, polyester film with a thickness of 12 micrometers by which biaxial extension was carried out was obtained, heat-treating for 5 seconds with the film temperature of 185 **. The obtained film showed the outstanding characteristic as it was shown in Table 1.

[0061]

[Table 1]

【表 1】

樹脂 A	成分	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7
	T _m (°C)	254	254	255	254	256	240	255
	重量%	80	80	85	80	70	60	80
樹脂 B	成分	PBT	PBT/I	PBT	PPT	PBT	PBT/DA	PBT/I
	T _m (°C)	223	209	223	220	223	190	209
	重量%	18	15	5	20	30	40	20
変性 P B T	T _m (°C)	160	221	219	-	-	-	-
	ポリエーテル 共重合率 (重量%)	70	5	23	-	-	-	-
	重量%	2	5	10	-	-	-	-
変形回復率		62	54	57	52	52	52	53
T _{meta} (°C)		185	190	205	202	185	178	172
β 分散	ピーク温度 (°C)	-52	-49	-54	-50	-55	-60	-48
	損失弾性率 (E')	300	380	240	590	400	500	280
	ピーク温度と半値温 度との差の絶対値	40	40	28	37	45	50	34
破断強度 (MPa)	MD	180	200	260	175	210	150	250
	TD	200	210	270	190	230	145	270
弾性率 (GPa)	MD	3.0	3.2	4.1	3.4	3.2	1.8	4.2
	TD	3.2	3.3	4.2	3.6	3.5	1.9	4.3
破断伸度 (%)	F _{MD}	150	125	120	150	120	180	110
	F _{TD}	130	130	110	140	110	190	110
	F _{MD} + F _{TD}	280	255	230	290	230	370	220
150°C 熱収縮率 (%)	MD	2.5	3.0	3.6	2.5	3.2	2.0	4.6
	TD	3.0	3.5	3.6	3.0	4.0	2.2	4.8
面配向係数		0.153	0.140	0.165	0.130	0.147	0.118	0.160
固有粘度 (dl/g)		0.70	0.68	0.68	0.68	0.70	0.82	0.78
耐ピンホール特性-1 評価 (ピンホール個数)		A (0)	B (3)	B (5)	B (3)	B (4)	B (4)	C (9)
耐ピンホール特性-2 評価 (突き刺し強度kg/mm)		A (30)	A (29)	A (32)	A (26)	A (30)	B (22)	A (34)
成形性		A	A	B	A	B	B	B

In addition, PET which is as follows [cable address / in the above-mentioned table] :. Polyethylene terephthalate PPT:.. Polypropylene terephthalate PBT:.. Polybutylene terephthalate PET/I:.. Isophthalic acid copolymerization polyethylene terephthalate PBT/DA:.. dimer acid copolymerization polybutylene terephthalate PBT/I:isophthalic acid copolymerization polybutylene terephthalate Tm:melting point Tmeta: - - sub endothermic peak temperature F_{MD} : resulting from heat treatment -- degree of breaking extension

F_{TD} : of a longitudinal direction -- in the cross direction, a breaking extension degree. (Example 2)

Polyethylene terephthalate as polyester (A) 80 % of the weight, Using 5 % of the weight of with 15 % of the weight and a melting point of 221 °C denaturation PBT as polyester (B), 10 mol of isophthalic acid copolymerization polybutylene terephthalate was adjusted so that spherical silica particles with a mean particle diameter of 1.2 micrometers might be contained 0.012% of the weight. Having supplied the single screw extruder and carrying out electrostatic impression after the regurgitation from the usual cap, after carrying out vacuum drying of the polymer chip at 120 °C for 6 hours, cooling solidification was carried out on the mirror plane cooling drum, and the unstretched film was obtained. this unstretched film -- it extending to a longitudinal direction at the extension temperature of 85 °C, extending 3.0 times crosswise at 120 °C after 3.0 time extension and within a tenter, and with a non-adhering silicone roll (hardness of 73 degrees), [rank second and] By carrying out crosswise relaxed 4%, polyester film with a thickness of 15 micrometers by which biaxial extension was carried out was obtained, heat-treating for 5 seconds with the film temperature of 190 °C. The obtained film showed the outstanding characteristic as it was collectively shown in Table 1.

(Example 3) Polyethylene terephthalate as polyester (A) 85 % of the weight, Polybutylene terephthalate was adjusted so that a condensation silica particle with a mean particle diameter of 1.5 micrometers might be contained for the denaturation PBT with a melting point of 219 °C 0.03% of the weight 5% of the weight, using 10 % of the weight as polyester (B). Having supplied the single screw extruder and carrying out electrostatic impression after the regurgitation from the usual cap, after carrying out vacuum drying of the polymer chip at 120 °C for 6 hours, cooling solidification was carried out on the mirror plane cooling drum, and the unstretched film was obtained. this unstretched film -- it extending to a longitudinal direction at the extension temperature of 85 °C, extending 3.8 times crosswise at 110 °C after 3.8 time extension and within a tenter, and with a non-adhering silicone roll (hardness of 80 degrees), [rank second and] By carrying out crosswise relaxed 4%, polyester film with a thickness of 20 micrometers by which biaxial extension was carried out was obtained, heat-treating for 8 seconds with the film temperature of 205 °C. The obtained film showed the outstanding characteristic as it was collectively shown in Table 1.

(Example 4) Polypropylene terephthalate was used for polyethylene terephthalate as polyester (A), and 20 % of the weight was used as polyester (B) 80% of the weight, and it adjusted so that an alumina particle with a mean particle diameter of 0.2 micrometer might be contained 0.05% of the weight. Having supplied the single screw extruder and carrying out electrostatic impression after the regurgitation from the usual cap, after carrying out vacuum drying of the polymer chip at 150 °C for 3 hours, cooling solidification was carried out on the mirror plane cooling drum, and the unstretched film was obtained. this unstretched film -- it extending to a longitudinal direction at the extension temperature of 90 °C, extending 3.1 times crosswise at 120 °C after 3.0 time extension and within a tenter, and with a non-adhering silicone roll (hardness of 73

degrees), [rank second and] By carrying out crosswise relaxed 4%, polyester film with a thickness of 15 micrometers by which biaxial extension was carried out was obtained, heat-treating for 5 seconds with the film temperature of 202 **. The obtained film showed the outstanding characteristic as it was collectively shown in Table 1.

(Example 5) Polybutylene terephthalate was used for polyethylene terephthalate as polyester (A), and 30 % of the weight was used as polyester (B) 70% of the weight, and it adjusted so that spherical silica particles with a mean particle diameter of 0.8 micrometer might be contained 0.012% of the weight. Having supplied the single screw extruder and carrying out electrostatic impression after the regurgitation from the usual cap, after carrying out vacuum drying of the polymer chip at 150 ** for 3 hours, cooling solidification was carried out on the mirror plane cooling drum, and the unstretched film was obtained. this unstretched film -- it extending to a longitudinal direction at the extension temperature of 95 **, extending 2.9 times crosswise at 115 ** after 2.9 time extension and within a tenter, and with a non-adhering silicone roll (hardness of 80 degrees), [rank second and] By carrying out crosswise relaxed 3%, polyester film with a thickness of 10 micrometers by which biaxial extension was carried out was obtained, heat-treating for 5 seconds with the film temperature of 185 **. The obtained film showed the outstanding characteristic as it was collectively shown in Table 1.

(Example 6) 6 mol of isophthalic acid copolymerization polyethylene terephthalate as polyester (A) 60 % of the weight, Using 40 % of the weight as polyester (B), 17 mol of dimer acid copolymerization polybutylene terephthalate was adjusted so that spherical silica particles with a mean particle diameter of 1.2 micrometers might be contained 0.012% of the weight. Having supplied the single screw extruder and carrying out electrostatic impression after the regurgitation from the usual cap, after carrying out vacuum drying of the polymer chip at 150 ** for 3 hours, cooling solidification was carried out on the mirror plane cooling drum, and the unstretched film was obtained. this unstretched film -- it extending to a longitudinal direction at the extension temperature of 85 **, extending 2.6 times crosswise at 120 ** after 2.7 time extension and within a tenter, and with a non-adhering silicone roll (hardness of 73 degrees), [rank second and] By carrying out crosswise relaxed 4%, polyester film with a thickness of 25 micrometers by which biaxial extension was carried out was obtained, heat-treating for 5 seconds with the film temperature of 178 **. The obtained film showed the outstanding characteristic as it was collectively shown in Table 1.

(Example 7) 10 mol of isophthalic acid copolymerization polybutylene terephthalate was used for polyethylene terephthalate as polyester (A), and 20 % of the weight was used as polyester (B) 80% of the weight, and it adjusted so that a condensation silica particle with a mean particle diameter of 1.5 micrometers might be contained 0.03% of the weight. Having supplied the single screw extruder and carrying out electrostatic impression after the regurgitation from the usual cap, after carrying out vacuum drying of the polymer chip at 150 ** for 3 hours, cooling solidification was carried out on the mirror plane cooling drum, and the unstretched film was obtained. this unstretched film -- it extending to a longitudinal direction at the extension temperature of 82 **, extending 3.8 times crosswise at 110 ** after 3.8 time extension and within a tenter, and with a non-adhering silicone roll (hardness of 80 degrees), [rank second and] By carrying out crosswise relaxed 4%, polyester film with a thickness of 30 micrometers by which biaxial extension was carried out was obtained, heat-treating for 5 seconds with the film temperature of 172 **. The obtained film showed the outstanding characteristic as it was collectively shown in Table 1.

(Comparative example 1) Using 100 % of the weight as polyester, polyethylene terephthalate was adjusted

so that a condensation silica particle with a mean particle diameter of 1.5 micrometers might be contained 0.03% of the weight. Having supplied the single screw extruder and carrying out electrostatic impression after the regurgitation from the usual cap, after carrying out vacuum drying of the polymer chip at 150 °C for 3 hours, cooling solidification was carried out on the mirror plane cooling drum, and the unstretched film was obtained. this unstretched film -- it extending to a longitudinal direction at the extension temperature of 100 °C, extending 3.1 times crosswise at 120 °C after 3.0 time extension and within a tenter, and with a non-adhering silicone roll (hardness of 80 degrees), [rank second and] By carrying out crosswise relaxed 4%, polyester film with a thickness of 20 micrometers by which biaxial extension was carried out was obtained, heat-treating for 5 seconds with the film temperature of 230 °C. This example from which the weight section of resin (A) and (B) separated from the range of this invention was inferior to pinhole-characteristics-proof-1 (GERUBO test) as the obtained film was shown in Table 2.

[0062]

[Table 2]

【表 2】

		比較例 1	比較例 2	比較例 3
樹脂 A	成分	PET	PET	PET
	T _m (°C)	253	254	254
	重量%	100	40	95
樹脂 B	成分	-	PBT/I	PBT
	T _m (°C)	-	209	223
	重量%	-	60	5
変性 PBT	T _m (°C)	-	-	-
	ポリエーテル共重合率 (重量%)	-	-	-
	重量%	-	-	-
変形回復率		51	50	53
T _{meta} (°C)		230	180	220
β 分散	ピーク温度 (°C)	-42	-65	-45
	損失弾性率 (E'')	410	540	180
	ピーク温度と半値温度との差の絶対値	48	52	25
破断強度 (MPa)	MD	195	90	320
	TD	195	100	340
弾性率 (GPa)	MD	3.1	1.5	4.8
	TD	3.3	1.4	4.9
破断伸度 (%)	F _{MD}	210	170	65
	F _{TD}	180	180	70
	F _{MD} + F _{TD}	390	350	135
150°C 熱収縮率 (%)	MD	1.2	2.3	8.0
	TD	1.3	2.4	8.2
面配向係数		0.128	0.080	0.173
固有粘度 (dl/g)		0.65	0.70	0.68
耐ピンホール特性-1 評価 (ピンホール個数)		C (58)	B (4)	破断
耐ピンホール特性-2 評価 (突き刺し強度 kg/mm)		A (25)	C (9)	A (39)
成形性		A	B	成形不可

In addition, PET which is as follows [cable address / in the above-mentioned table] : Polyethylene terephthalate PBT: polybutylene terephthalate PBT/I: isophthalic acid copolymerization polybutylene terephthalate T_m: melting point T_{meta}: -- sub endothermic peak temperature F_{MD}: resulting from heat treatment -- degree of breaking extension F_{TD}: of a longitudinal direction -- in the cross direction, a

breaking extension degree. (Comparative example 2) 10 mol of isophthalic acid acid copolymerization polybutylene terephthalate was used for polyethylene terephthalate as polyester (A), and 60 % of the weight was used as polyester (B) 40% of the weight, and it adjusted so that spherical silica particles with a mean particle diameter of 1.2 micrometers might be contained 0.012% of the weight. Having supplied the single screw extruder and carrying out electrostatic impression after the regurgitation from the usual cap, after carrying out vacuum drying of the polymer chip at 150 °C for 3 hours, cooling solidification was carried out on the mirror plane cooling drum, and the unstretched film was obtained. this unstretched film -- it extending to a longitudinal direction at the extension temperature of 70 °C, extending 2.0 times crosswise at 110 °C after 1.8 time extension and within a tenter, and with a non-adhering silicone roll (hardness of 73 degrees), [rank second and] By carrying out crosswise relaxed 4%, polyester film with a thickness of 30 micrometers by which biaxial extension was carried out was obtained, heat-treating for 5 seconds with the film temperature of 180 °C. This example from which the weight section of resin (A) and (B), breaking strength, Young's modulus, and a plane orientation coefficient separated from the range of this invention was inferior to pinhole-characteristics-proof-2 (thrusting intensity) and a moldability as the obtained film was collectively shown in Table 2.

(Comparative example 3) Polybutylene terephthalate was used for polyethylene terephthalate as polyester (A), and 5 % of the weight was used as polyester (B) 95% of the weight, and it adjusted so that a condensation silica particle with a mean particle diameter of 1.5 micrometers might be contained 0.03% of the weight. Having supplied the single screw extruder and carrying out electrostatic impression after the regurgitation from the usual cap, after carrying out vacuum drying of the polymer chip at 150 °C for 3 hours, cooling solidification was carried out on the mirror plane cooling drum, and the unstretched film was obtained. this unstretched film -- it extending to a longitudinal direction at the extension temperature of 85 °C, extending 4.3 times crosswise at 110 °C after 4.2 time extension and within a tenter, and with a non-adhering silicone roll (hardness of 73 degrees), [rank second and] By carrying out crosswise relaxed 4%, polyester film with a thickness of 80 micrometers by which biaxial extension was carried out was obtained, heat-treating for 5 seconds with the film temperature of 220 °C. As the obtained film is collectively shown in Table 2 The loss modulus of beta distribution, the absolute value of the difference of the peak temperature of beta distribution, and the half-the-price temperature of a loss modulus, This example from which Young's modulus, the degree of breaking extension, the 150 °C heat shrinkage rate, and the plane orientation coefficient separated from the range of this invention was inferior to pinhole-characteristics-proof-1 (GERUBO test) and a moldability.

[0063]

[Effect of the Invention]While having the ductility which is not in the conventional PET film by this invention, the biaxial orientation polyester film for fabricating operations excellent in working characteristics, such as heat resistance, dimensional stability, and a moldability, can be provided.

[Translation done.]